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(54) **Multilayer ceramics from silicate esters.**

(57) Disclosed are materials produced by diluting in a solvent a preceramic mixture of a partially hydrolyzed silicate ester which is applied to a substrate and heated to form a ceramic. One or more ceramic coatings containing silicon + carbon, silicon + nitrogen, or silicon + carbon + nitrogen can be applied over the ceramic SiO_2 coating. A CVD or PECVD top coating can be applied for further protection. The invention is particularly useful for coating electronic devices.

EP 0 270 241 A3

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EUROPEAN SEARCH REPORT

Application Number

EP 87 30 9620

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,A	EP-A-0 206 717 (NISSAN CHEMICAL INDUSTRIES LTD.) * page 1, lines 3-8; claims 1,8 *	1	C 04 B 41/50 C 04 B 41/52 H 01 L 21/316 H 01 L 21/56 H 01 L 23/28 C 04 B 41/89
A	EP-A-0 011 738 (IBM CORP.) * claims 1-4, 12 *	1	
A	GB-A-2 125 423 (WESTERN ELECTRIC COMPANY INC.) * page 1, lines 67-90 *	1	
A	DE-A-1 812 977 (CORNING GLASS WORKS)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 04 B 35/00 C 04 B 41/00 H 01 L 21/00 H 01 L 23/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	26-10-1989	KESTEN W.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(54) **Multilayer ceramics from silicate esters.**

(57) This invention relates to materials produced by diluting in a solvent a preceramic mixture of a partially hydrolyzed silicate ester which is applied to a substrate and ceramified by heating. One or more ceramic coatings containing silicon carbon, silicon nitrogen, or silicon carbon nitrogen can be applied over the ceramified SiO_2 coating. A CVD or PECVD top coating can be applied for further protection. The invention is particularly useful for coating electronic devices.

EP 0 270 241 A2

MULTILAYER CERAMICS FROM SILICATE ESTERS

Electronic devices, to be serviceable under a wide variety of environmental conditions, must be able to withstand moisture, heat, and abrasion resistance, among other stresses. A significant amount of work has been reported directed toward the preparation of coatings for electronic devices which can increase the reliability of the devices. None of the conventional coatings available today, including ceramic and metal packaging, can perform well enough by itself to protect an electronic device against all environmental stresses.

A common cause of failure of electronic devices is microcracks or voids in the surface passivation of the semiconductor chip allowing the introduction of impurities. Thus, a need exists for a method which will overcome the formation of microcracks, voids or pinholes in inorganic coatings of electronic devices.

Passivating coatings on electronic devices can provide barriers against ionic impurities, such as chloride ion (Cl-) and sodium ion (Na+), which can enter an electronic device and disrupt the transmission of electronic signals. The passivating coating can also be applied to electronic devices to provide some protection against moisture and volatile organic chemicals.

Amorphous silicon (hereinafter a-Si) films have been the subject of intense research for various applications in electronic industries, however, the use of a-Si films for environmental or hermetic protection of electronic devices is unknown. A number of possible processes have been previously disclosed for forming a-Si films. For instance, for producing films of amorphous silicon, the following deposition processes have been used: chemical vapor deposition (CVD), plasma enhanced CVD (PECVD), reactive sputtering, ion plating and photo-CVD, etc. Generally, the plasma enhanced CVD process is industrialized and widely used for depositing a-Si films.

Known to those skilled in the art is the utility of substrate planarization as an interlayer within the body of an electronic device and between the metallization layers. Gupta and Chin (Microelectronics Processing, Chapter 22, "Characteristics of Spin-On Glass Films as a Planarizing Dielectric", pp349-65, American Chemical Society, 1986) have shown multilevel interconnect systems with isolation of metallization levels by conventional interlevel dielectric insulator layers of doped or undoped SiO_2 glass films. However CVD dielectric films provide only at best a conformal coverage of substrate features which is not conducive to continuous and uniform step coverage by an overlying metallization layer. The poor step coverage results in discontinuous and thin spots in the conductor lines causing degradation of metallization yields as well as device reliability problems. Spin-on glass films have been utilized to provide interlayer isolation between the metallization layers, the top layer of which is later patterned by lithographic techniques. Topcoat planarization on the surface of an electronic device as opposed to planarizing interlevel dielectric layers, however, is unknown.

Under the teachings of the prior art, a single material most often will not suffice to meet the ever increasing demands of speciality coating applications, such as those found in the electronics industry. Several coating properties such as microhardness, moisture resistance, ion barrier, adhesion, ductility, tensile strength, thermal expansion coefficients, etc., need to be provided by successive layers of different coatings.

Silicon and nitrogen-containing preceramic polymers, such as silazanes have been disclosed in various patents, including U.S. Patent No. 4,404,153, issued September 13, 1983, to Gaul, wherein there is disclosed a process for preparing R'_3 SiNH-containing silazane polymers by contacting and reacting chlorine-containing disilanes with $(R'_3\ Si)_2$ NH where R' is vinyl, hydrogen, an alkyl radical of 1 to 3 carbon atoms or the phenyl group. Gaul also teaches therein the use of the preceramic silazane polymers to produce silicon-carbon-nitrogen-containing ceramic materials.

Gaul in U.S. Patent 4,312,970, issued January 26, 1982, obtained ceramic materials by the pyrolysis of preceramic silazane polymers, which polymers were prepared by reacting organochlorosilanes and disilazanes.

Gaul in U.S. Patent 4,340,619, issued July 20, 1982, obtained ceramic materials by the pyrolysis of preceramic silazane polymers, which polymers were prepared by reacting chlorine-containing disilanes and disilazanes.

Cannady in U.S. Patent 4,540,803, issued September 10, 1985, obtained ceramic materials by the pyrolysis of preceramic silazane polymers, which polymers were prepared by reacting trichlorosilane and disilazanes.

The instant invention relates to the enhancement of the protection of electronic devices by the low temperature formation of thin multilayer ceramic or ceramic-like coatings on the surface of the device. What has been discovered is a method of forming one or more silicon-and nitrogen-containing ceramic or ceramic-like coatings for the protection of electronic devices.

The instant invention relates to a process for

the low temperature formation of multilayer and monolayer coatings for the protection of electronic devices. The monolayer coating for the protection of electronic devices consists of ceramified silicon dioxide layer deposited from a solution of preceramic silicate polymer. The dual-layer coatings of the present invention consist of (1) a coating prepared by depositing on an electronic device a solvent solution of a material containing silicon and oxygen, wherein upon heat treatment the material ceramifies to form a SiO_2 -containing material, and (2) a topcoating of silicon-containing material, or silicon nitrogen-containing material, or silicon carbon-containing material, or silicon carbon nitrogen-containing material.

The first layer applied over the electronic device is a SiO_2 -containing planarizing and passivating coating that is applied by known coating techniques, including flow coating, spin coating, dip coating and spray coating of an electronic device. The second layer is a hermetic-type barrier coating of silicon-containing material derived from the CVD, PECVD or metal assisted CVD of halosilanes, halopolysilanes, halodisilanes, silanes or mixtures thereof with or without alkanes. The metal-assisted CVD process is claimed in the parallel U.S. patent application Serial No. 835,029, filed February 28, 1986, in the name of Sudarsanan Varaprath and entitled "Silicon-Containing Coatings and a Method for Their Preparation".

The instant invention also relates to the formation of a three layer coating system for the protection of electronic devices wherein the first layer is an SiO_2 -containing planarizing coating obtained from a solvent solution of a material containing silicon and oxygen, wherein, upon heat treatment, the material ceramifies to form an SiO_2 -containing material. Such materials can include, but are not limited to, organic orthosilicates, $Si(OR)_4$, or condensed esters of the type $(RO)_3SiOSi(OR)_3$, and any other source of SiOR such that upon hydrolysis and subsequent pyrolysis a material of essentially SiO_2 is produced. Thus, materials containing carbon, such as SiOC-containing materials, can be included in this group if the carbon-containing group is hydrolyzable under the thermal conditions so as to volatilize out leaving essentially SiO_2 . The second layer, used for passivation, is a ceramic or ceramic-like coating obtained by the ceramification of a preceramic SiN-containing polymer coating, or is a silicon nitrogen-containing, silicon carbon nitrogen-containing, or silicon carbon-containing layer deposited by thermal, UV, CVD, plasma enhanced CVD, or laser techniques. The third layer in the three layer coatings of the present invention is a top coating of (a) silicon-containing material applied by CVD, plasma enhanced CVD, or metal assisted CVD of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof, or (b) silicon carbon-containing material, applied by CVD or plasma enhanced CVD of a silane, alkylsilane, halosilane, halodisilane, halopolysilane, or mixtures thereof, and an alkane or alkylsilane, or (c) silicon nitrogen-containing material applied by CVD or plasma enhanced CVD of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof, and ammonia, or (d) silicon carbon nitrogen-containing material applied by CVD or plasma enhanced CVD of hexamethyldisilazane or a mixture of silanes, alkylsilanes, alkanes and ammonia.

The instant invention relates to the discovery that silicon dioxide (SiO_2 -containing) ceramic or ceramic-like coatings derived from the ceramification of a silicate ester solution can be applied onto electronic devices and integrated circuits to provide protection of the devices or circuits from the environment.

The instant invention further relates to the discovery that these silicon dioxide (SiO_2 -containing) ceramic or ceramic-like coatings can be coated with various silicon, carbon and nitrogen-containing materials for the protection of electronic devices as well as other integrated circuits.

In the instant invention, by "ceramic-like" is meant those pyrolyzed materials which are not fully free of residual carbon and/or hydrogen but which are otherwise ceramic-like in character. By "hydrolyzed silicate ester" in the instant invention is meant any SiO_2 -containing material, as described above, which has been hydrolyzed or partially hydrolyzed by treatment with, for example, aqueous, basic or acidic conditions. By "electronic device" in the instant invention is meant devices including, but not limited to, electronic devices, silicon based devices, gallium arsenide devices, focal plane arrays, opto-electronic devices, photovoltaic cells, optical devices and the like. The coatings of the instant invention are also useful as dielectric layers, doped dielectric layers to produce transistor-like devices, pigment loaded binder systems containing silicon to produce capacitors and capacitor-like devices, multilayer devices, 3-D devices, silicon-on-insulator (SOI) devices, super lattice devices and the like.

The instant invention also relates to a process for the formation of silicon-containing top coatings for ceramic or ceramic-like coated electronic devices whereby the topcoat is prepared by plasma enhanced CVD, metal assisted CVD (MACVD) techniques, or other CVD techniques.

The instant invention also relates to a process for forming on a substrate a ceramic or ceramic-like SiO_2 coating which process comprises (A) coating an electronic device with a planarizing coating by means of diluting a hydrolyzed or par-

tially hydrolyzed silicate ester to low solids with a solvent and applying the diluted hydrolyzed or partially hydrolyzed silicate ester solution to an electronic device; (B) drying the diluted hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device; (C) ceramifying the hydrolyzed or partially hydrolyzed silicate ester to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like planarizing SiO_2 coating on the device.

In addition, the instant invention relates to a process for forming on a substrate a multilayer, ceramic or ceramic-like coating which process comprises (A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution, drying the diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution so as to evaporate the solvent and thereby deposit a hydrolyzed or partially hydrolyzed silicate ester preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester preceramic coating to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like SiO_2 coating and (B) applying to the ceramic or ceramic-like SiO_2 coated device a silicon-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halodisilane, halopolysiloxane or mixture thereof in the vapor phase, at a temperature between 200 and 600°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like, coating thereon is obtained. The process for applying the planarizing or passivating coatings on the electronic device can be, but is not limited to, flow coating, spin coating, spray or dip coating techniques.

The instant invention further relates to a process for forming on a substrate a multilayer, ceramic or ceramic-like, coating which process comprises (A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution, drying the diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution so as to evaporate the solvent and thereby deposit a hydrolyzed or partially hydrolyzed silicate ester preceramic material coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester preceramic material coating to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and (B) applying to the ceramic or ceramic-like coated device a silicon nitrogen-containing coating by means of applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, and heating the coated device to a temperature of 200 to 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating on the electronic device.

The instant invention also relates to a process for forming on a substrate a multilayer, ceramic or ceramic-like, coating which process comprises (A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution, drying the diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution so as to evaporate the solvent and thereby deposit a hydrolyzed or partially hydrolyzed silicate ester preceramic material coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester preceramic material coating to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and (B) applying to the ceramic or ceramic-like coated device a silicon carbon-containing coating by means of decomposing in a reaction chamber a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof, and a material selected from the group consisting of alkanes of one to six carbon atoms, alkylsilanes, and alkylhalosilanes, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like, coating thereon is obtained.

The instant invention further relates to a process for forming on a substrate a multilayer, ceramic or ceramic-like, coating which process comprises (A) coating an electronic device with a ce-

ramic or ceramic-like coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution, drying the diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution so as to evaporate the solvent and thereby deposit a hydrolyzed or partially hydrolyzed silicate ester preceramic material coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester preceramic material coating to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and (B) applying to the ceramic or ceramic-like coated device a passivating coating which comprises a silicon nitrogen-containing material by means of diluting with a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the preceramic silicon nitrogen-containing polymer solution, drying the preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature of 200 to 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and (C) applying to the ceramic or ceramic-like coated device a silicon-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halodisilane or halopolysilane or mixture thereof in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic like, coating thereon is obtained.

The invention also relates to a process for forming on a substrate a multilayer, ceramic or ceramic-like, coating which process comprises (A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution, drying the diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution so as to evaporate the solvent and thereby deposit a hydrolyzed or partially hydrolyzed silicate ester preceramic material coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester preceramic material coating to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and (B) applying to the ceramic or ceramic-like coated device a passivating coating which comprises a silicon nitrogen-containing material by means of diluting with a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and (C) applying to the ceramic or ceramic-like coated device a silicon nitrogen-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halopolysilane, or mixture thereof and ammonia, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like, coating thereon is obtained.

The instant invention further relates to a process for forming on a substrate a multilayer, ceramic or ceramic-like, coating which process comprises (A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution, drying the diluted hydrolyzed or partially hydrolyzed silicate ester preceramic material solution so as to evaporate the solvent and thereby deposit a hydrolyzed or partially hydrolyzed silicate ester preceramic material coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester preceramic material coating to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and (B) applying to the ceramic or ceramic-like coated device a passivating coating which comprises a silicon nitrogen-containing material by means of diluting with a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and

(C) applying to the ceramic or ceramic-like coated device a silicon carbon-containing coating by means of decomposing in a reaction chamber a silane, alkylsilane, halosilane, halodisilane, halopolysilane, or mixtures thereof, and an alkane of one to six carbon atoms or an alkylsilane, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like, coating thereon is obtained.

In the instant invention, a hydrolyzed or partially hydrolyzed silicate ester preceramic material, for example, ethyl orthosilicate, is diluted (e.g. 0.1 to 10 weight %) with a solvent such as isopropyl alcohol or ethanol. The diluted preceramic solvent solution is then coated onto an electronic device and the solvent allowed to evaporate by drying at ambient conditions. The process of coating the diluted preceramic polymer solution onto the electronic device can be, but is not limited to, spin coating, dip coating, spray coating, or flow coating, The hydrolyzed or partially hydrolyzed silicate ester preceramic material is oxidized in air, or in water vapor and air, to an SiO_2 -containing material. By this means is deposited a preceramic polymer coating which is ceramified by heating the coated device, for example, for approximately one hour at 400°C. A thin ceramic or ceramic-like planarizing coating of less than 2 microns (or approximately 3000 to 5000 A) is thus produced on the device. The planarizing coating thus produced is then coated with a passivating silicon nitrogen-containing ceramic or ceramic-like coating of the present invention or with a CVD applied silicon-containing coating, silicon carbon-containing coating, or silicon nitrogen-containing coating or a combination of these coatings.

The second and passivating silicon nitrogen-containing layer of the composite coatings in the instant invention provides resistance against ionic impurities. Preceramic SiN-containing polymers suitable for use in this present invention are well known in the art, including, but not limited to, silazanes, disilazanes, polysilazanes, cyclic silazanes, and other silicon nitrogen-containing materials. The preceramic silicon nitrogen-containing polymers suitable for use in this invention must be capable of being converted to a ceramic or ceramic-like material at elevated temperatures. Mixtures of preceramic silazane polymers and/or other silicon-and nitrogen-containing materials may also be used in this invention. Examples of preceramic silazane polymers or polysilazanes suitable for use in this invention include polysilazanes as described by Gaul in U.S. Patents 4,312,970 (issued January 26, 1982); 4,340,619 (issued July 20, 1982); 4,395,460 (issued July 26, 1983); and 4,404,153 (issued September 13, 1983). Suitable polysilazanes also include those described by Haluska in U.S. Patent 4,482,689 (issued November 13, 1984) and by Seyferth et al. in U.S. Patent 4,397,828 (issued August 9, 1983), and Seyferth et al. in U.S. Patent 4,482,669 (issued November 13, 1984). Other polysilazanes suitable for use in this invention are disclosed by Cannady in U.S. Patents 4,540,803 (issued September 10, 1985); 4,535,007 (issued August 13, 1985), and 4,543,344 (issued September 24, 1985); and by Baney et al. in U.S. Patent Application Serial No. 652,939, filed September 21, 1984. Also suitable for use in this invention are dihydridosilazane polymers prepared by the reaction of H_2SiX_2, where X = a halogen atom, and NH_3. These $(H_2SiNH)_n$ polymers are well known in the art, but have not been used for the protection of electronic devices. (See, for example, Seyferth, U.S. Patent No. 4,397,828, issued August 9, 1983).

Also to be included as preceramic silicon nitrogen-containing polymer materials useful within the scope of the present invention are the novel preceramic polymers derived from the reaction between cyclic silazanes and halogenated disilanes, and also the novel preceramic polymers derived from the reaction between cyclic silazanes and halosilanes. These materials are disclosed and claimed in patent applications of Serial Nos. 926,145, titled "Novel Preceramic Polymers Derived From Cyclic Silazanes And Halogenated Disilanes And A Method For Their Preparation", and 926,607, titled "Novel Preceramic Polymers Derived From Cyclic Silazanes And Halosilanes And A Method For Their Preparation", respectively, filed in the name of Loren A. Haluska. The above-described novel preceramic silicon nitrogen-containing polymers derived from cyclic silazanes and halosilanes and/or halogenated disilanes are also useful for the protection of any substrate able to withstand the temperatures necessary for ceramification of said preceramic polymers. Still other silicon-and nitrogen-containing materials may be suitable for use in the present invention.

In the preparation of the passivating layer of the coatings of the instant invention, a preceramic polymer containing silicon and nitrogen is diluted to low solids (e.g., 0.1 to 10 weight %) in a solvent such as toluene or n-heptane. The diluted silicon nitrogen-containing polymer solvent solution is coated (by any method discussed above) onto the electronic device previously coated with the ceramified SiO_2 -containing material and the solvent allowed to evaporate by drying in an inert or ammonia-containing atmosphere. By this means is deposited a preceramic polymer coating which is ceramified by heating the coated device for approximately one hour at temperatures up to 400°C.

under argon. Thin ceramic or ceramic-like passivating coatings of less than 2 microns (or approximately 3000 to 5000 A) are thus produced on the devices.

A preferred temperature range for ceramifying or partially ceramifying the silicon nitrogen-containing preceramic polymer is from 200 to 400°C. A more preferred temperature range for ceramifying the silicon nitrogen-containing preceramic polymer is from 300 to 400°C. However, the method of applying the heat for the ceramification or partial ceramification of the silicon nitrogen-containing coating is not limited to conventional thermal methods. The silicon nitrogen-containing polymer coatings useful as planarizing and passivating coatings in the instant invention can also be cured by other radiation means, such as, for example, exposure to a laser beam. However, the present invention is not limited to ceramification temperatures below 400°C. Ceramification techniques utilizing temperatures up to and including at least 1000°C. will be obvious to those skilled in the art, and are useful in the present invention where the substrate can withstand such temperatures.

By "cure" in the present invention is meant coreaction and ceramification or partial ceramification of the starting material by heating to such an extent that a solid polymeric ceramic or ceramic-like coating material is produced.

Alternatively, in the three layer coating of the instant invention, the second and passivating coating can be selected from the group consisting of silicon nitrogen-containing material, silicon carbon nitrogen-containing material, and silicon carbon-containing material. The silicon nitrogen-containing material is deposited by the CVD or plasma enhanced CVD of the reaction product formed by reacting silane, halosilanes, halopolysilanes, or halodisilanes and ammonia. The silicon carbon-containing material is deposited by the CVD or plasma enhanced CVD of the reaction product formed by reacting silane, alkylsilane, halosilanes, halopolysilanes, or halodisilanes and an alkane of one to six carbon atoms or an alkylsilane. The silicon carbon nitrogen-containing material is deposited by the CVD or PECVD of hexamethyldisilazane or by the CVD or PECVD of mixtures comprising a silane, alkylsilane, alkane, and ammonia.

The silicon-containing third layer or topcoat of the composite coatings of the present invention can be obtained at relatively low reaction temperature by the metal-assisted CVD process claimed in the parallel U.S. patent application Serial No. 835,029, mentioned supra, or by conventional non-metal assisted CVD or plasma enhanced CVD techniques. The metal-assisted CVD process is particularly suited for the deposition of coatings from $SiCl_4$, $SiBr_4$, $HSiI_3$, $HSiCl_3$ and $HSiBr_3$.

The choice of substrates and devices to be coated by the instant invention is limited only by the need for thermal and chemical stability of the substrate at the lower decomposition temperature in the atmosphere of the decomposition vessel.

The process of the present invention provides onto the electronic devices coated with ceramified hydrolyzed or partially hydrolyzed silicate ester material and ceramified silicon nitrogen-containing material, a silicon-containing topcoating of a thickness which can be varied as desired depending upon the concentration of the silicon halides that are being reduced. The top coatings of the instant invention can be deposited by any known state-of-the-art technique.

Coatings produced by the instant invention possess low defect density and are useful on electronic devices as protective coatings, as corrosion resistant and abrasion resistant coatings, as temperature and moisture resistant coatings, and as a diffusion barrier against ionic impurities such as Na^+ and Cl^-. The silicon nitrogen-containing ceramic or ceramic-like coatings of the instant invention are also useful as interlevel dielectrics within the body of the electronic device and between the metallization layers, thereby replacing spin-on glass films.

The coatings of the present invention are useful for functional purposes in addition to protection of electronic devices from the environment. The coatings of the present invention are also useful as dielectric layers, doped dielectric layers to produce transistor-like devices, pigment loaded binder systems containing silicon to produce capacitors and capacitor-like devices, multilayer devices, 3-D devices, silicon-on-insulator (SOI) devices, and super lattice devices.

Another unique aspect of the coatings produced by the present invention is their transparency to electromagnetic radiation. Thus, a particular advantage of the coatings of the present invention is utilization on focal plane arrays, photovoltaic cells, or opto-electronic devices in which electromagnetic radiation can pass into or emanate from the coated device.

Example 1

A solution of 8.6 milliliters of ethyl orthosilicate, 8.6 milliliters of ethanol, 2.8 milliliters of water and one drop of 5% hydrochloric acid was heated at 60°C. for thirty minutes, then was diluted with 60 milliliters of ethanol. After standing overnight at room temperature, the solution was flow coated onto aluminum panels, the coating was air dried 10 minutes, and then heat cured in air at 400° for 2

1/2 hours. After cooling to room temperature, the coatings were found to be clear and transparent. Thin ceramic or ceramic-like SiO_2 -containing coatings of less than 2 microns (or approximately 3000 to 5000 A) were thus produced on the panels.

Example 2

An RCA 4011 CMOS electronic device was flow coated with a 1 weight percent solution of the coating solution of Example 1. The coating was air dried 10 minutes, then heat cured for 1 hour at 400°C. By this process was produced on the electronic device a ceramic or ceramic-like SiO_2 -containing planarizing coating of less than 2 microns (or approximately 4000 A).

Example 3

A preceramic silazane polymer, prepared by the method of Cannady in Example 1 in U.S. Patent No. 4,540,803, was diluted to 1.0 weight per cent in toluene. The preceramic silazane polymer solvent solution was then flow coated onto the electronic device coated by the method of Example 2 and the solvent was allowed to evaporate by drying in the absence of air. By this means was deposited a preceramic polymer passivating coating which was ceramified by heating the coated device for approximately one hour at 400°C. under argon. Thin silicon-nitrogen-containing ceramic or ceramic-like passivating coatings of less than 2 microns (or approximately 3000 Angstroms) were thus produced on the devices.

Example 4

Using the procedure of Example 3, a preceramic silazane polymer containing about 5 per cent titanium, prepared by the method of Haluska in Example 13 in U.S. Patent No. 4,482,689, was flow coated onto the electronic device and the solvent allowed to evaporate by drying. By this means was deposited a preceramic polymer coating which was ceramified by heating the coated device for approximately one hour at temperatures up to 400°C. under argon. Thin silicon nitrogen-containing ceramic or ceramic-like passivating coatings of less than 2 microns (or approximately 3000 Angstroms) were thus produced on the devices.

Example 5

Using the procedure of Example 3, a preceramic silazane polymer, prepared by the method of Gaul in Example 1 in U.S. Patent No. 4,395,460, was coated onto the electronic device and the solvent allowed to evaporate by drying. By this means was deposited a preceramic polymer coating which was ceramified by heating the coated device for approximately one hour at temperatures up to 400°C. under argon. Thin silicon nitrogen-containing ceramic or ceramic-like passivating coatings of less than 2 microns (or approximately 3000 Angstroms) were thus produced on the devices.

Example 6

A 1-2 weight % solution in diethyl ether of dihydridosilazane polymer, prepared by the method of Seyferth in Example 1 in U.S. Patent 4,397,828, was flow coated onto a CMOS device previously coated by the method of Example 1, above. The coated device was heated in nitrogen for one hour at 400C. The coating and pyrolysis treatment did not adversely affect the device function, as determined by a CMOS circuit tester. The coated device withstood 0.1M NaCl exposure for over four and one half hours before circuit failure. A nonprotected CMOS device will fail to function after exposure to a 0.1M NaCl solution for less than one minute.

Example 7

The electronic devices coated with the planarizing and/or passivating coatings of Examples 1 through 6 were then overcoated with the barrier coats as follows; Hexafluorodisilane, 500 Torr, was placed in a Pyrex glass reaction container along with an electronic device, previously coated with a ceramified silicon nitrogen-containing material. The hexafluorodisilane was transferred to the glass container in such a manner as to preclude exposure to the atmosphere. The reaction container was then attached to a vacuum line, the contents evacuated, and the container thoroughly heated under vacuum with a gas-oxygen torch. The container was sealed with a natural gas-oxygen torch and heated in an oven for 30 minutes at a temperature of approximately 360°C. During this time, the hexafluorodisilane starting material decomposed and formed a silicon-containing topcoat on the previously coated electronic device. The reaction byproducts mixtures of various halosilanes, and any unreacted starting material were removed by evac-

uation after the container had been reattached to the vacuum line. The ceramic coated electronic device, onto which the decomposed hexafluorodisilane starting material had deposited a silicon-containing topcoating, was then removed.

Example 8

Using the procedure described in Example 7, dichlorodisilane was thermally decomposed in the presence of the ceramic or ceramic-like SiO_2 and silicon nitrogen coated electronic device. An amorphous silicon-containing topcoat was thereby deposited onto the ceramic or ceramic-like coated electronic device. The coated device was tested and all electronic circuits were operable.

Claims

1. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(I) (A) coating an electronic device with a planarizing coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester with a solvent and applying the diluted hydrolyzed or partially hydrolyzed silicate ester solution to an electronic device; (B) drying the hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device; (C) ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce a ceramic or ceramic-like planarizing coating.

(II) applying to the ceramic or ceramic-like planarizing coating a passivating coating selected from the group consisting of (i) a silicon nitrogen-containing coating, (ii) a silicon carbon-containing coating, and (iii) a silicon carbon nitrogen-containing coating, wherein the silicon nitrogen-containing coating is applied onto the planarizing coating of the electronic device by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of ammonia, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of ammonia, (c) ceramification of a silicon and nitrogen-containing preceramic polymer; and wherein the silicon carbon nitrogen-containing coating is applied onto the planarizing coating of the electronic device by a means selected from the group consisting of (1) chemical vapor deposition of hexamethyldisilazane, (2) plasma enhanced chemical vapor deposition of hexamethyldisilazane, (3) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, and (4) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia; and wherein the silicon carbon-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, and (ii) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, to produce the passivating ceramic or ceramic-like coating, and

(III) applying to the passivating ceramic or ceramic-like coating a silicon-containing coating selected from the group consisting of (i) silicon coating, (ii) silicon carbon-containing coating, (iii) silicon nitrogen-containing coating, and (iv) silicon carbon nitrogen-containing coating, wherein the silicon coating is applied onto the passivating coating by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof, or (c) metal assisted chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof, and wherein the silicon carbon-containing coating is applied by a means selected from the group consisting of (1) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, (2) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane; and wherein the silicon nitrogen-containing coating is deposited by a means selected from the group consisting of (A) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of ammonia, (B) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of ammonia, and (C) ceramification of a silicon and nitrogen-containing preceramic polymer, and

wherein the silicon carbon nitrogen-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of hexamethyldisilazane, (ii) plasma enhanced chemical vapor deposition of hexamethyldisilazane, (iii) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, and (iv) plasma ennanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, to produce the silicon-containing coating, whereby a multilayer, ceramic or ceramic-like, coating is obtained on the electronic device.

2. A process for forming on an electronic device a dual layer, ceramic or ceramic-like coating which process comprises:

(I) (A) coating an electronic device with a planarizing coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester with a solvent and applying the diluted hydrolyzed or partially hydrolyzed silicate ester solution to an electronic device: (B) drying the diluted hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device; (C) ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce a ceramic or ceramic-like planarizing coating; and

(II) applying to the ceramic or ceramic-like planarizing coating a passivating coating selected from the group consisting of (i) a silicon-containing coating, (ii) a silicon nitrogen-containing coating, (iii) a silicon carbon-containing coating, and (iv) a silicon carbon nitrogen-containing coating, wherein the silicon-containing coating is applied onto the planarizing coating of the electronic device by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof, or (c) metal assisted chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof; wherein the silicon nitrogen-containing coating is applied onto the ceramic or ceramic-like coated electronic device by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of ammonia, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of ammonia, (c) ceramification of a silicon and nitrogen-containing preceramic polymer; and wherein the silicon carbon nitrogen-containing coating is applied onto the planarizing coating of the electronic device by a means selected from the group consisting of (1) chemical vapor deposition of hexamethyldisilazane, (2) plasma enhanced chemical vapor deposition of hexamethyldisilazane, (3) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, and (4) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia; and wherein the silicon carbon-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, and (ii) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, to produce the passivating ceramic or ceramic-like coating, whereby a dual layer, ceramic or ceramic-like coating is obtained on the electronic device.

3. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at a temperature of 200 to 1000°C. to produce a ceramic or ceramic-like coating, and

(B) applying to the ceramic or ceramic-like coated device a silicon-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halodisilane, halopolysilane, or mixture thereof, and ammonia, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated

device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

4. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a silicon nitrogen-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halodisilane, halopolysiloxane or mixture thereof, and ammonia, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

5. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a silicon carbon-containing coating by means of decomposing in a reaction chamber a silane, alkylsilane, halosilane, halodisilane, halopolysilane, or mixture thereof, and an alkane of one to six carbon atoms or an alkylsilane, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

6. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce a ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a silicon carbon nitrogen-containing coating by means of decomposing in a reaction chamber hexamethyldisilazane in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

7. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a silicon carbon nitrogen-containing coating by means of chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six , carbon atoms or an alkylsilane and further in the presence of ammonia, to produce the silicon-containing coating, whereby a multilayer, ceramic or ceramic-like, coating is obtained on the electronic device.

8. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a silicon carbon nitrogen-containing coating by means of plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, to produce the silicon-containing coating, whereby a multilayer, ceramic or ceramic-like coating is obtained on the electronic device.

9 . A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce a ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature of 200 to 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic silicon nitrogen-containing coating, and

(C) applying to the ceramic coated device a silicon-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halodisilane or mixture thereof in the vapor phase, at a temperature between 200 and 600°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

10. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a ceramic or ceramic-like coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air or in water vapor and air to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic silicon nitrogen-containing coating, and

(C) applying to the ceramic or ceramic-like coated device a silicon nitrogen-containing coating by means of decomposing in a reaction chamber a silane, halosilane, halodisilane, halopolysilane or mixture thereof, and ammonia, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

11. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and

(C) applying to the ceramic or ceramic-like coated device a silicon carbon-containing coating by means of decomposing in a reaction chamber a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof, and an alkane of one to six carbon atoms or an alkylsilane, in the vapor phase, at a temperature between 200 and 1000°C., in the presence of the ceramic or ceramic coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

12. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or, partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and,

(C) applying to the ceramic or ceramic-like coated device a silicon carbon nitrogen-containing coating by means of chemical vapor deposition of hexamethyldisilazane, in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

13. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coating a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an

inert or ammonia-containing atmosphere to produce the ceramic or ceramic like silicon nitrogen-containing coating, and,

(C) applying to the ceramic or ceramic-like coating a silicon carbon nitrogen-containing coating by means of plasma enhanced chemical vapor deposition of hexamethyldisilazane, in the presence of the ceramic or ceramic-like coated device, whereby an electronic device containing a multilayer, ceramic or ceramic-like coating thereon is obtained.

14. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce the ceramic or ceramic-like coating, and.

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and,

(C) applying to the ceramic or ceramic-like coated device a silicon carbon nitrogen-containing coating by means of chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, to produce the silicon carbon nitrogen-containing coating, thereby a multilayer, ceramic or ceramic-like, coating is obtained on the electronic device.

15. A process for forming on an electronic device a multilayer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed, silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device at temperatures of 200 to 1000°C. to produce a ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the diluted preceramic silicon nitrogen-containing polymer solution, drying the diluted preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the ceramic or ceramic-like silicon nitrogen-containing coating, and,

(C) applying to the ceramic or ceramic-like coated device a silicon carbon nitrogen-containing coating by means of plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, to produce the silicon-containing coating, whereby a multilayer, ceramic or ceramic-like, coating is obtained on the electronic device.

16. A process for forming on an electronic device a dual layer, ceramic or ceramic-like coating which process comprises:

(A) coating an electronic device with a coating by means of diluting a hydrolyzed or partially hydrolyzed silicate ester preceramic material with a solvent, coating an electronic device with said diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution, drying the diluted preceramic hydrolyzed or partially hydrolyzed silicate ester solution so as to evaporate the solvent and thereby deposit a preceramic coating on the electronic device, ceramifying the hydrolyzed or partially hydrolyzed silicate ester in air, or in water vapor and air, to silicon dioxide by heating the coated device to a temperature between 200 and 1000°C. to produce the ceramic or ceramic-like coating, and,

(B) applying to the ceramic or ceramic-like coated device a passivating coating comprising a silicon nitrogen-containing material produced by means of diluting in a solvent a preceramic silicon nitrogen-containing polymer, coating the ceramic or ceramic-like coated device with the preceramic silicon nitrogen-containing polymer solution, drying the preceramic silicon nitrogen-containing polymer solution so as to evaporate the solvent and thereby deposit a preceramic silicon nitrogen-containing coating on the ceramic or ceramic-like coated electronic device, and heating the coated device to a temperature between 200 and 1000°C. in an inert or ammonia-containing atmosphere to produce the passivating silicon nitrogen-containing coating, thereby producing a dual layer, ceramic or ceramic-like coating on the electronic device.

17. A method of coating a substrate with a ceramic or ceramic-like silicon nitrogen-containing material, wherein said method comprises the steps of:

(1) diluting with a solvent a silicon and nitrogen-containing preceramic polymer produced by reacting a cyclic silazane or a mixture of cyclic silazanes with a silicon-containing material selected from the group consisting of halodisilanes and halosilanes;

(2) coating a substrate with the diluted preceramic polymer solvent solution;

(3) drying the diluted preceramic polymer solvent solution in the absence of air so as to evaporate the solvent and thereby deposit a preceramic polymer coating on the substrate; and

(4) heating the coated substrate in the absence of air to produce a ceramic or ceramic-like coated substrate.